

ENERGIES OF ATOMIZATION FROM POPULATION ANALYSES ON HÜCKEL WAVE FUNCTIONS

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Abstract

Three-dimensional Hückel molecular orbital (MO) calculations have been performed on a series of molecules made from the atoms H, C, N, O, F, and Cl. Mulliken population analyses on the ground-state wave functions for the valence electrons have been related empirically to the observed energies of atomization. This is most successful when the compounds are first divided into two classes, those containing carbon and those without carbon. The population analysis is cast in the form of a charge density-bond order matrix, ρ , for all the valence electrons and for the π -electrons separately, in the case of planar molecules. The energy of atomization, E_{atom} , is then approximated as:

$$E_{\text{atom}} = A \cdot \sum_{\mu < \nu} \rho_{\mu\nu} + B \sum_{\mu < \nu} \rho_{\mu\nu}^{\pi} + C \sum_{\mu < \nu} \Delta X_{\mu\nu}^2$$

where $\rho_{\mu\nu}$ are interatomic overlap populations and $\rho_{\mu\nu}^{\pi}$ are the corresponding π -overlap populations. The $\Delta X_{\mu\nu}$ are electronegativity differences for bonded atoms. The second summation is over net positive values only. For 40 compounds not containing carbon the observed E_{atom} are fit with a mean deviation of 11.1 kcal/mole. Only constants A and C are needed. For the 22 compounds of carbon that were studied all three constants are needed, B being negative. The best fit requires a weighted function of $\Delta X_{\mu\nu}^2$ and even then the mean deviation is nearly twice that found for the compounds not containing carbon.

Introduction

The present study was initiated to see to what extent empirical molecular orbital (MO) theories of the Hückel type can provide information on the thermodynamic stability of a hypothetical unknown compound. The test, of course, has to be made on known compounds. Our interests have centered on compounds involving atoms such as N, O, F, and Cl but compounds with C and H have also been included. The results thus far have been encouraging.

It was from the papers of Lipscomb, Lohr, Hoffmann, et al¹⁻⁶⁾ that we first learned of their work on an "extended" Hückel theory for polyatomic molecules. We also benefited from a visit to Harvard to discuss this work before their computer program became generally available. Our computer program is based on what we learned from them at that time and on our experience since then in applying it to our particular types of molecules.

The other major influence in the work has come from the papers of Mulliken and his co-workers, in particular the 1955 series⁷⁾ on population analysis of LCAO-MO wave functions and its relation to energies of atomization. As was suggested by Mulliken,⁸⁾ we have attempted to relate the calculated overlap populations to the energy of atomization for the molecule, with corrections for the polarity of the bonds.

Three-Dimensional Hückel Theory

The theory¹⁻⁶⁾ will be outlined for molecules having n atoms with a total of P valence-shell electrons. We seek a set of molecular orbitals (LCAO-MO's), ψ , that are linear combinations of atomic orbitals centered on the atoms in the molecule. Since we shall not ignore overlap, the geometry of the molecule must be known or one must guess it. The molecule is placed in an arbitrary cartesian coordinate system and the coordinates of each atom are determined. s and p Slater-type orbitals (STO's) make up the basis and as indicated above we restrict ourselves to the valence-shell electrons for each of the atoms in the molecule. The STO's have the following form for the radial part of the function:⁹⁾¹⁰⁾

$$R(r) = N r^m \exp(-\zeta r/a_H) \quad (1)$$

where N is a normalization factor
 $m = 0$ for 1 s electrons, 1 for 2 s or 2 p electrons and 2 for 3 s or 3 p electrons
 ζ = orbital exponent
 a_H = Bohr radius = 0.529175 A.

The mathematical representation of the basis is needed only for the calculation of the overlap matrix, which it is assumed gives a good representation of the tendency to form a bond.

If Φ is a row vector of the atomic orbitals that make up the basis: $\Phi_1, \Phi_2, \dots, \Phi_N$, then the molecular orbitals are given by an $N \times N$ matrix, Ψ ,

$$\Psi = \Phi C \quad (2)$$

C is a transformation matrix that satisfies the equations:

$$HC = SC\epsilon \quad (3)$$

and

$$C'SC = I \quad (C'_{ij} = C_{ji}) \quad (4)$$

ϵ is a diagonal matrix of the orbital energies and S is the overlap matrix of the atomic orbitals,¹⁰⁾

$$S_{ij} = \int \Phi_i \Phi_j d\tau \quad (5)$$

It reflects the known or assumed geometry of the molecule.

The Hamiltonian matrix, H , is approximated in the following way. The diagonal elements are effective valence-state ionization potentials for the s and p electrons of the atom in question. The off-diagonal elements are calculated according to one of the following options:¹²⁾

$$1. H_{ij} = -K_1 (H_{ii} H_{jj})^{\frac{1}{2}} S_{ij} \quad (6)$$

$$2. H_{ij} = K_2 \frac{(H_{ii} + H_{jj})}{2} S_{ij} \quad (7)$$

K_1 and K_2 are adjustable parameters having an empirical value of ca 2.0.

A population analysis⁷⁾ is performed and a "charge density-bond order" matrix is calculated. The latter is an $n \times n$ matrix whose diagonal elements are "gross atomic populations" (its trace is P). The off-diagonal elements are "overlap populations". It is convenient to define a matrix, \underline{R} , of dimensions $N \times N$ whose elements are

$$R_{ij} = \sum_k n(k) C_{ik} C'_{kj}.$$

$n(k)$ is the occupation number of the k^{th} MO, i.e., 2, 1 or 0. The elements of the charge density-bond order matrix, $\underline{\rho}$, can then be written:⁷⁾

$$\rho_{\mu\mu} = \sum_i (\underline{SR})_{ii} \quad (8)$$

$$\rho_{\mu\nu} = 2 \sum_{j>i}^{\mu\nu} S_{ij} R_{ij} \quad (9)$$

The \sum^{μ} means that the sum goes over the atomic orbitals associated with the μ^{th} atom. Similarly, $\sum^{\mu\nu}$ means that the sum includes all terms where orbital i is on the μ^{th} atom and orbital j is on the ν^{th} atom. As indicated above, it can be shown that: $\text{trace}(\underline{SR}) = P$.

The individual diagonal elements of $\underline{\rho}$ can be associated with the atomic charges, q_{μ} :

$$q_{\mu} = p_{\mu} - \rho_{\mu\mu} \quad (10)$$

where p_{μ} is the number of valence-shell electrons contributed by the μ^{th} atom.

If the molecule has a π -system that is completely separated by symmetry from the σ -system a separate π -electron ρ -matrix is also calculated from the π -MO's.

The H_{ii} 's are actually a function of the appropriate q_{μ} and when these are different from zero it is possible to make $\underline{H}(q)$ consistent with the calculated q_{μ} 's by an iterative procedure. The \underline{S} matrix is also a function of q through the dependence of the orbital exponents on q and these are also altered periodically during the course of the perturbation.

Parameters for the Calculations

The values for the valence-state ionization potentials, I_v , and their dependence on charge were obtained from the work of Hinze and Jaffé.¹³⁾¹⁴⁾ The values that have given the best overall results are those for ionization from s^2 or p^2 configurations. From the original tables of Hinze, Whitehead and Jaffé,¹⁴⁾ values of I_v were calculated for the neutral atom, A , and for A^+ and A^- . These values never quite lie on a straight line so a simple parabola was used to interpolate for any intermediate value of the charge. Table 1 gives the values used for the atoms of interest and the equations as a function of charge.

Orbital exponents for calculations (Table 1) have been taken from the paper of Clementi and Raimondi.¹¹⁾ Their dependence on charge has been assumed to be that given by Slater's formulas for orbital exponents.⁹⁾ Various

values of K and the option of the arithmetic or geometric mean (equations 6 and 7) have been tried and the results cited here are all for the geometric mean (6) and for $K_1 = 2.0$.

Results

Sixty-two molecules made up of H, C, N, O, F and Cl have been used to test various relationships between calculated quantities and the observed energies of atomization, E_{atom} . Of these, 40 contained no carbon atoms and 22 contained carbon. Multiple regression techniques were used to test the significance of various relationships of the form:

$$E_{\text{atom}} = A \cdot \sum_{\mu < \nu} \rho_{\mu\nu} + B \cdot \sum_{\mu < \nu}^+ \rho_{\mu\nu}^{\pi} + C \cdot f(\Delta X_{\mu\nu}). \quad (11)$$

The sums of off-diagonal elements from the calculated charge density-bond order matrix, ρ , were considered both as net positive and net negative elements separately and combined. No significant advantage to separating them was found. All π -electron overlap populations are included in the first term, but the net positive ones only are considered separately as a second term. The last term introduces some function of the polarity of the molecule, $f(\Delta X_{\mu\nu})$. Approximate Coulomb energies were calculated for each molecule from the gross atomic charges, q_{μ} . These were tried as a third term but they were only moderately successful as a polarity function. Much more successful was one of the Pauling¹⁵⁾ type:

$$f^P(\Delta X_{\mu\nu}) = \sum_{\text{bonds}} \Delta X_{\mu\nu}^2 \quad (12)$$

where $\Delta X_{\mu\nu}$ is the difference between the electronegativities of the bonded atoms, μ and ν . A scale of electronegativities similar to Pauling's was determined so as to give a best fit to the data. This scale is given in Table 2; Pauling's values¹⁵⁾ are also given for comparison. The optimum value of C (in equation 11), however, was always less than half the value of 30 kcal/mole that was used by Pauling in deriving his electronegativity scale.¹⁵⁾

A second closely-related polarity function has some advantages for the compounds of carbon:

$$f^C = f^P (1/b \sum_{\mu < \nu}^+ \rho_{\mu\nu}); \quad (13)$$

b is the number of bonds in the molecule and the sum is over net positive values of overlap population. f^C , then, is the Pauling function, f^P , weighted by the average bond overlap population. This was found to be important for strong covalent bonds such as occur in CO_2 but its use for weakly covalent bonds such as those in ClF_3 leads to an underestimation of their stability. An advantage to an altered set of electronegativities was also found. This set of electronegativities is also given in Table 2.

Table 3 gives a summary of the results of using equation 11 as a representation of the energies of atomization for the sixty-two test molecules. Results are quoted for both polarity functions, f^P and f^C . When the entire set of molecules is tested, f^C seems to be the preferred function; however, f^P is definitely superior for the compounds without carbon and f^C and the

alternate electronegativities are superior for the C compounds. For extrapolations to other molecules it would seem desirable to use f^P for compounds without carbon and f^C and the alternate electronegativities for those with carbon. It is interesting that the A-value is considerably larger for carbon compounds than for others. This, plus the need for a relatively large negative value for B, must reflect the particular stability of the tetrahedral hybrid orbitals used by carbon. Tables 4 and 5 give the results for the sixty-two compounds each calculated according to the preferred formula.

Only a few calculations have thus far been performed on unknown compounds, or on compounds whose energy of formation has not been reported. Our estimates for these are given in Table 6. For NCl_3 , which is known to be unstable we estimate a positive energy of formation of +34 kcal while NF_3 which is stable is known to have a negative value of -31.9. CH_3NCl_2 and $(\text{CH}_3)_2\text{NCl}$ both of which are relatively stable have calculated energies of formation of -2 kcal/mole and -6 kcal/mole respectively. The recently-reported¹⁶ molecule ClF_5 , assumed to have a square pyramidal structure analogous to BrF_5 , is predicted to have an energy of formation of -48 kcal/mole and the hypothetical molecule N_6 , assumed to be an analogue of benzene, is predicted to have a positive energy of formation of +109 kcal/mole. It would thus be quite unstable relative to 3 moles of N_2 , which probably explains why the compound has not been made. It would appear that were it not for repulsions between the lone pairs, the molecule might be stable.

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Table 1. ORBITAL EXPONENTS, ζ , AND EQUATIONS FOR H_{ii}

$$H_{ii} = -I_V - Aq_i - Bq_i^2$$

Atom	Orbital	ζ	I_V	A	B
H	1s	1.20 ^{a)}	13.20 ^{a)}	12.85	-
C	2s	1.6083	19.52	11.75	1.15
	2p	1.5679	9.75	10.86	1.55
N	2s	1.9237	25.58	13.31	1.78
	2p	1.9170	12.38	13.09	1.54
O	2s	2.2458	32.30	15.35	1.49
	2p	2.2266	14.61	14.77	2.17
F	2s	2.5638	39.42	17.27	2.21
	2p	2.5500	18.31	16.62	1.85
Cl	3s	2.3561	25.23	11.48	0.70
	3p	2.0387	13.92	10.44	0.24

a) I_V is altered so that the ionization potential of H_2 is moderately well reproduced, and ζ to agree with values used in the best simple LCAO treatments of H_2 .

Table 2. EFFECTIVE ATOMIC ELECTRONEGATIVITIES

Atom	Electronegativity		Pauling Scale ¹⁵⁾
	(a)	(b)	
H	1.70	1.7	2.1
C	-	2.3	2.5
N	3.10	2.85	3.0
O	3.45	3.45	3.5
F	4.08	3.95	4.0
Cl	2.90	3.0	3.0

(a) Determined for compounds not containing carbon. They are indicated as being significant to ± 0.05 to 0.1 unit.

(b) For compounds of carbon. Significance is ca 0.1 unit.

Table 3. CONSTANTS IN EQUATIONS FOR EATOM
(SEE EQUATION 11) AND STANDARD DEVIATIONS IN KCAL/MOLE

Calculation I uses f^P ; Calculation II uses f^C .

All but one use set (a) of electronegativities from Table 2.

Calculation Type	Number of Molecules	Standard Deviation	Maximum Deviation	A	B	C
I	62	25.2	69.2	132.7 ± 1.9	-48.5 ± 6.3	10.35 ± 0.95
II		22.7	51.8	132.6 ± 1.6	-56.9 ± 5.5	15.2 ± 1.2
I*	40a)	11.1	22.3	116.0 ± 1.1	--	$11.63 \pm .94$
II		13.7	40.4	116.4 ± 1.4	--	17.3 ± 1.9
I	22b)	24.4	63.8	138.2 ± 2.0	-57.8 ± 6.5	9.8 ± 1.0
II		20.0	49.2	137.6 ± 1.7	-65.2 ± 5.2	14.2 ± 1.2
II*	(c)	17.3	38.8	136.6 ± 1.5	-61.5 ± 4.5	16.8 ± 1.2

* Preferred formula for extrapolation.

a) All molecules without carbon.

b) Compounds of carbon; in each case maximum deviation is for CO_2 .

c) Using alternate set (b) of electronegativities from Table 2.

TABLE 4. CALCULATED AND OBSERVED ENERGIES OF ATOMIZATION (ENAT) FOR COMPOUNDS WITHOUT CARBON. MEAN DEVIATION= 11.1 KCAL/MOLE. ELECTRONEGATIVITIES - H= 1.70, C= 2.30, N= 3.10, O= 3.45, F= 4.08, CL= 2.90

COMPOUND	SUM OVERLAP POPULATIONS ALL VALUES	+PI ONLY	SUM BOND (DELTA X)**2	ENAT(OBS) KCAL/MOLE	ENAT(CALC) KCAL/MOLE
H2	0.794	0.	0.	110.5	92.1
N2	1.791	0.905	0.	229.3	207.7
O2	0.854	0.170	0.	121.4	99.1
F2	0.281	0.	0.	39.0	32.6
CL2	0.484	0.	0.	59.7	56.1
NH3	2.105	0.	5.880	300.8	312.6
OH	0.685	0.	3.062	107.4	115.1
H2O	1.303	0.	6.125	234.3	222.4
HF	0.612	0.	5.664	141.5	136.9
HCL	0.717	0.	1.440	107.3	99.9
NO	1.205	0.417	0.122	153.4	141.2
N2O	2.482	0.918	0.122	272.6	289.3
NO2	1.951	0.420	0.245	229.0	229.1
N2O3	3.303	0.750	0.367	394.5	387.4
N2O4	4.110	0.765	0.490	472.0	482.4
N2O5	4.634	0.728	0.735	536.2	546.0
FN0	1.528	0.376	1.083	211.6	189.8
CLN0	1.505	0.373	0.162	192.8	176.5
FN02	2.277	0.330	1.205	278.1	278.1
CLN02	2.268	0.375	0.285	262.9	266.4
FON02	2.681	0.344	0.764	316.6	319.9
NF	0.543	0.077	0.960	71.0	74.2
NF2	1.046	0.074	1.921	144.0	143.7
T-N2F2	2.060	0.402	1.921	251.4	261.3
C-N2F2	2.054	0.403	1.921	254.8	260.6
T-N2F4	2.438	0.	3.842	316.5	327.5
G-N2F4	2.438	0.	3.842	316.5	327.5
NF3	1.489	0.	2.881	206.0	206.2
O3	1.336	0.249	0.	149.7	155.0
OF	0.392	0.	0.397	53.0	50.1
F2O	0.739	0.	0.794	95.0	94.9
F2O2	1.227	0.	0.794	156.5	151.6
F2O3	1.680	0.	0.794	219.0	204.1
OCL	0.573	0.	0.302	65.0	70.0
CL2O	0.812	0.	0.605	103.0	101.2
CL02	1.140	0.	0.605	126.6	139.3
CL03	1.527	0.	0.907	177.0	187.7
CL2O7	3.347	0.	2.420	437.0	416.4
CLF	0.368	0.	1.392	62.3	58.9
CLF3	0.622	0.	4.177	128.8	120.7

TABLE 5. CALCULATED AND OBSERVED ENERGIES OF ATOMIZATION (ENAT) FOR COMPOUNDS OF CARBON. MEAN DEVIATION= 17.3 KCAL/MOLE. ELECTRONEGATIVITIES - H= 1.70, C= 2.30, N= 2.85, O= 3.45, F= 3.95, CL= 3.00

COMPOUND	SUM OVERLAP ALL VALUES	POPULATIONS +PI ONLY	SUM WT BOND (DELTA X)**2	ENAT(OBS) KCAL/MOLE	ENAT(CALC) KCAL/MOLE
C2	1.738	0.934	0.	145.0	180.0
CH4	2.991	0.	1.164	420.0	428.1
C2H6	5.025	0.	1.740	710.7	715.5
C3H8	7.056	0.	2.319	1005.3	1002.7
C4H10	9.087	0.	2.899	1300.7	1289.8
C3	2.978	1.272	0.	329.5	328.6
CN	1.741	0.916	0.527	178.0	190.3
(CN)2	4.451	1.970	0.926	504.0	502.4
C4N2	7.197	3.132	0.913	801.7	805.8
FCN	2.434	0.997	3.737	310.5	333.9
CLCN	2.495	1.022	1.015	285.3	295.0
CO	1.554	0.790	2.055	206.0	198.2
CO2	2.619	1.053	3.527	391.0	352.2
C3O2	5.149	2.087	3.560	654.0	634.7
F2CO	2.489	0.459	5.885	429.4	410.5
CL2CO	2.485	0.470	2.067	346.8	345.2
CF	0.729	0.201	1.985	117.0	120.5
CF4	2.550	0.	7.397	476.1	472.3
C2F4	3.605	0.500	8.398	582.0	602.5
C2F6	4.325	0.	10.998	775.0	775.2
CCLF3	2.475	0.	5.805	424.0	435.4
CCL4	2.338	0.	1.336	318.5	341.8

Table 6. ESTIMATED ENERGIES OF ATOMIZATION AND
ENERGIES OF FORMATION FOR SOME MOLECULES

<u>Molecule</u>	<u>E_a (calc) kcal/mole</u>	<u>ΔE_{formation} kcal/mole</u>	<u>Known Stability</u>
NCl ₃	205	+34	unstable
CH ₃ NCl ₂	513	-2	stable
(CH ₃) ₂ NCl	824	-6	stable
NHF ₂	227	-18	stable
ClF ₅	175	-48	stable
N ₃ *	579	+109	unknown

* Assumed to be the aromatic analog of benzene with bond lengths equal to 1.29Å.